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Title: NEW ANION-EXCHANGE RESINS FOR IMPROVED
SEPARATIONS OF NUCLEAR MATERIALS

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FINAL REPORT
U.S. Department of Energy

**NEW ANION-EXCHANGE RESINS FOR IMPROVED SEPARATIONS OF
NUCLEAR MATERIALS**

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Executive Summary

The overall objective of this project was to develop a predictive capability that would enable us to design and implement new anion-exchange materials that selectively sorb metal complexes. Our approach was to extend the principles applied to optimization of chelating ligands (i.e., "preorganization," "bite size," and "chelate effect") to the weaker, more diffuse electrostatic interactions between complex anions and dicationic sites of anion-exchange resins. We have found that the resulting Quantitative Structure-Activity Relationship (QSAR) is useful in predicting the overall trend within a select series of bifunctional resins, and we hope to refine this methodology further to allow the *a priori* determination of ion-exchange behavior for a broad class of materials.

This project advances our ability to design improved ion-exchange systems by using calculational methods to narrow the range of materials that must be synthesized and tested. The concept of preorganizing a multifunctional anion-exchange site to obtain improved selectivity has been validated, and we have developed specific synthetic routes to new materials of this type. The concepts and new materials developed by this EMSP project address critical needs within DOE environmental management programs to remove radionuclides and other metal ions more efficiently from a variety of waste and process streams. More selective and efficient ion-exchange systems can provide faster throughput rates, reduced wastes, and lower capital equipment costs. Thus the project has effectively bridged the gap between fundamental research and needs-driven applied technology development.

So far, the new anion-exchange methodology and corresponding materials have found their greatest utility in removing americium from effluent of the nitric-acid plutonium recovery process. Reducing the total decay-heat in LANL cemented wastes is mandated by WIPP transportation and disposal requirements, and removal of excess americium moves many of these wastes from non-compliant to compliant status. Additionally, the improved resins are being investigated for Pu-238 purification since the high radiolytic activity of this isotope necessitates use of a material with facile and comprehensive sorption/desorption characteristics. While our resins also exhibit improved binding for Pu-239, their utility over commercial anion-exchange materials will depend upon cost/benefit analyses. A licensing agreement has been signed with an industrial firm to develop commercial applications of these new materials which should make them more cost-effective.

This project has developed significant fundamental knowledge that advances our ability to design improved ion-exchange systems more rapidly. It also has provided new materials that have applications in the near term. One patent has been issued on these new anion-exchange materials, another patent is expected to issue in the near future, and a patent disclosure is

presently being evaluated by the Laboratory. The first users would likely be industrial customers of Reilly Industries (licensing agreement), but the new materials would be available at essentially the same time for DOE applications. DOE customers that are likely to deploy these new anion exchangers include actinide processing operations at the Savannah River Site and Los Alamos National Laboratory.

Research on this project has involved eleven Texas Tech University personnel, including eight graduate students, two postdoctoral assistants, and one faculty member. Results obtained while supported by the DOE-EMSP grant will be incorporated into the theses and dissertations of two of the TTU graduate student coworkers. Efforts at LANL have involved various technical and support staff members. The postdoctoral associate brought in to do the molecular modeling for this project has since been hired as a full-time technical staff member and has engaged in interactions with numerous other technical projects.

Research Objectives

We are developing bifunctional anion-exchange resins that facilitate anion uptake by carefully controlling the structure of the anion receptor site. We are attempting to determine to what extent the precepts of "bite size," "preorganization," and "bidentate" have an appreciable impact upon electrostatic bonding interactions between metal ions and the resin sites. To the extent that these precepts do have a positive impact, we will develop new ion-exchange resins that interface the rapidly developing field of ion-specific chelating ligands with robust, commercial ion-exchange technology.

The overall objective of our research is to develop a predictive capability that will enable us to design and implement multi-functionalized anion-exchange materials that selectively sorb metal complexes of interest from targeted process, waste, and environmental streams. The following Focus Areas have described needs that would be favorably impacted by the new materials:

Nuclear Materials - Pu, Am or total alpha removal to <30 pCi/L before discharge to the environment, radionuclide removal (Pu, U, Am) from aqueous phases

Subsurface Contaminants - U and Tc in groundwater; U, Pu, Am, and Tc in soils

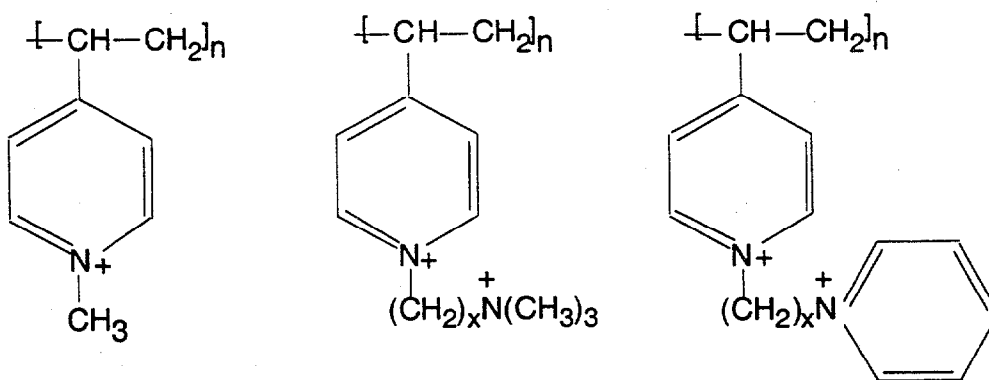
Mixed Waste - radionuclide partitioning, separation of RCRA metal ions from radioactive components to reduce volume of mixed waste

Tanks - actinide and Tc removal from supernatants and/or sludges

Methods and Results

We determine *actinide-complex speciation* in specific media, then *develop models* for the metal complex/functional site interactions *Synthesis* of multi-functional extractants and ion-exchange materials that implement key features of the optimized binding site, and *testing* of these materials, provide feedback to the modeling and design activities. To determine optimal binding site characteristics, we have combined empirical testing with theoretical modeling (applied in an iterative mode).

Resin materials that actively facilitate the uptake of actinide complexes from solution could display both improved selectivity and kinetic properties. Our primary implementation of the bifunctionality concept involves N-derivatization of pyridinium units from a base poly(4-vinylpyridine) resin with a second cationic site such that the two anion-exchange sites are linked by "spacer" arms of varying length and flexibility. Representative materials are presented below.



Methylated resins

HP18-Me = ca. 18% crosslinked, ~70% methylated, experimental resin

HPQTM = ca. 25% crosslinked, ~70% methylated

Bifunctional resins; $x = 3, 4, 5, 6$

HP18-(CH₂)_x-N(CH₃)₃ = ca. 18% crosslinked, ~70% alkylated

HP21-(CH₂)_x-N(CH₃)₃ = ca. 21% crosslinked, ~70% alkylated

HP21-(CH₂)_x-NC₅H₅ = ca. 21% crosslinked, ~70% alkylated

Actinide-complex speciation

The primary actinides of interest in nitrate solutions are plutonium (IV) and americium (III). Anion exchange from nitric acid is the most frequently used process used for the recovery of plutonium from a wide variety of residues and wastes in the DOE complex. While Pu(IV) binds strongly to the anion-exchange resin at high nitric acid concentrations and can be eluted with lower acid concentrations, the kinetics for sorption and desorption are extremely slow and adversely affect throughput rates. Spectroscopic studies of plutonium (IV) in nitric acid sorbed to ion-exchange media establish that the 12-coordinate hexanitrate complex is the species sorbed to anion-exchange sites, regardless of the Pu(IV) speciation in solution.¹⁻³ Of particular interest is the observation that Pu(IV) sorption onto the resin correlates best with the solution concentration of the uncharged tetranitrato complex, raising the possibility that Pu(IV) sorption occurs concurrently with the acquisition of two nitrate ligands (Figure 1). Individual monocationic sites of conventional anion-exchange resins are not optimally configured to either

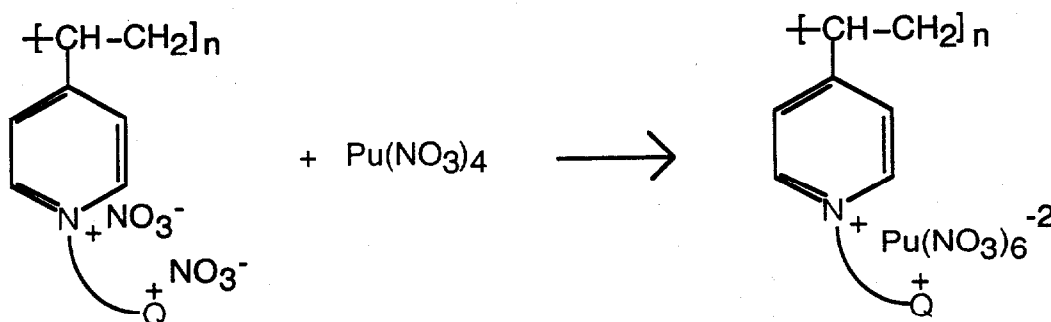


Figure 1. Schematic for facilitated uptake of $\text{Pu}(\text{NO}_3)_4$ onto preorganized bifunctional resin.

facilitate this process or to bind the final dianionic complex. Thus, we hypothesized that bifunctional resins could facilitate the uptake process, providing superior binding properties and selectivity for dianionic complexes and exhibiting enhanced kinetics for plutonium uptake from solution.

Refined formation constants for the various Pu-nitrate complexes have been determined for the mono- and di-nitrato complexes in constant ionic strength media (~2-20 N perchlorate/nitrate).^{4,5} As expected, in higher ionic strength media, the formation of the tetranitrato complex shifts to lower acid concentrations than in pure nitric acid. We have used this Pu(IV) data to expand our work on Am(III) uptake from high-salt media (see below).

Given the extremely slow kinetics of Pu uptake onto Reillex HPQ® (the methylated polyvinylpyridine resin currently used for plutonium processing at the Los Alamos Plutonium Facility), we could not be confident that the uptake behavior (i.e. the K_d curve) at 0.5, 2 and 6 hours corresponds to equilibrium conditions. More precise experiments (Figure 2) show that the uptake behavior at shorter times is reasonably indicative of equilibrium behavior in that 'short time' sorption and desorption behavior (from resin loaded at 7 M nitric acid) that is analogous to the equilibrium behavior. This helps provide support for the hypothesis that the plutonium on the anion-exchange resin is in equilibrium with the plutonium tetranitrato species in solution.

Americium is a primary contaminant in aged plutonium. Am(III), however, is less inclined to form anionic nitrate complexes in high acid media because of its lower charge density. Previous extraction technology for americium has focused on cation-exchange mechanisms, but the presence of large quantities of competing species, such as Fe(III), make this process very non-selective. Although anionic nitrate complexes for Am are not observed in pure nitric acid (a

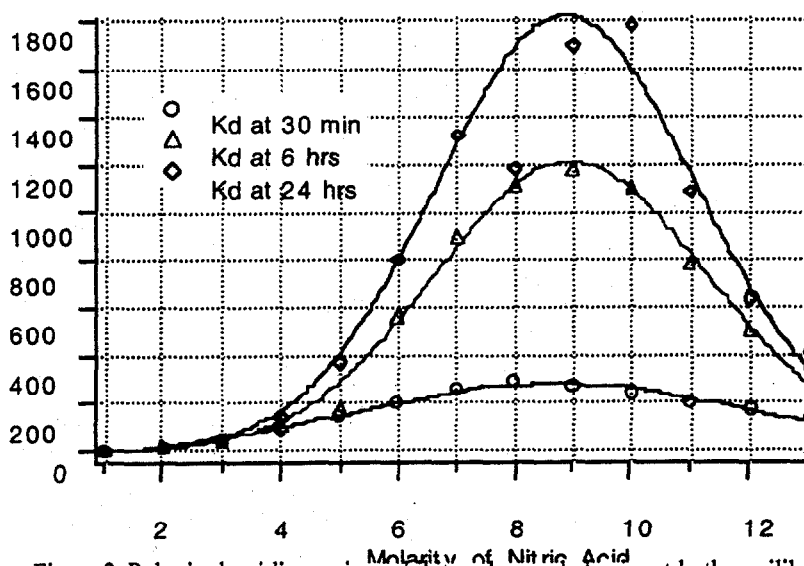


Figure 2. Polyvinylpyridine resins exhibit analogous behavior at both equilibrium (24 hrs) and pre-equilibrium (30 min. and 6 hrs) conditions.

feature exploited in plutonium processing), the concentrated effluents from nitric acid processing possess relatively higher nitrate and lower water activity – conditions which generally facilitate the formation of higher complexes. Under these conditions, anion exchange may provide an effective mechanism for the sorption of americium. Work with Nd(III), a non-radioactive analogue of Am(III) shows that for the same total nitrate concentration, trivalent metals form higher-order nitrate complexes in a calcium salt solution than in pure nitric acid (Figure 3).⁶ This chemistry is exploited in our use of our bifunctional anion-exchange resins for the removal of excess Am from LANL TA-55 pre-cementation solutions as outlined in the next section.⁷

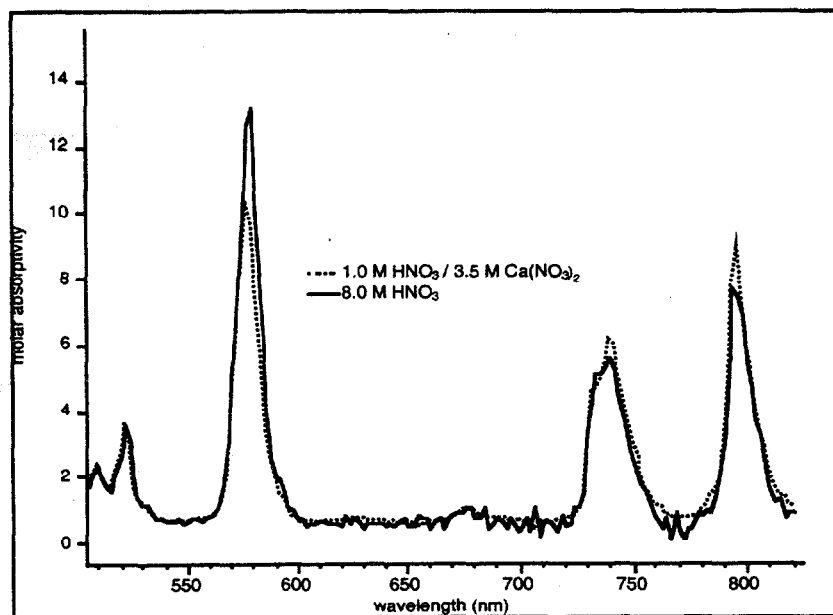


Fig. 3. Nd(III) in nitric acid and a salt solution. $[Nd] \sim 15 \text{ mM}$, $[NO_3] = 8.0 \text{ M}$

Synthesis and evaluation of bifunctional anion-exchange materials

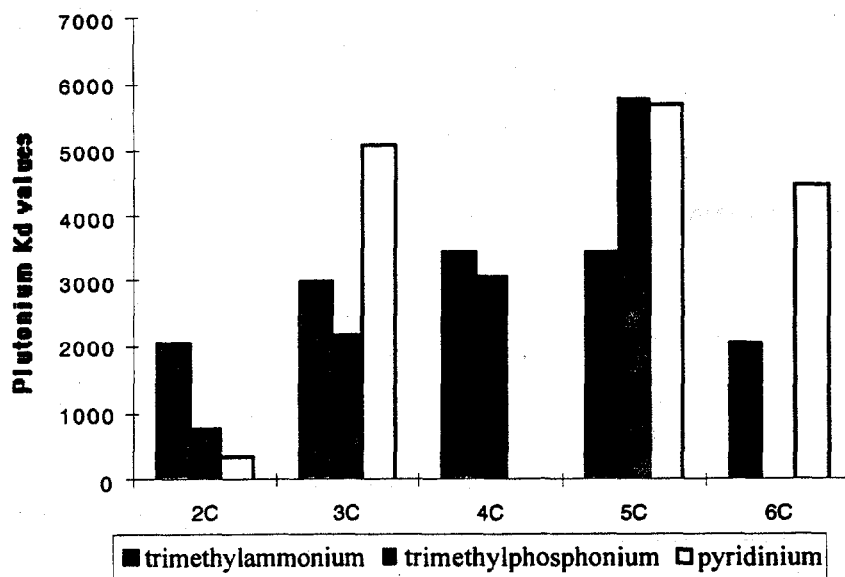
To prepare these new bifunctional resins, we needed to synthesize the appropriate asymmetric precursors. Reactions of 1, ω -bromoalkanes with trimethylamine generally form both mono- and disubstituted products. We developed a procedure which allows the monoquaternized ω -bromoalkyltrimethylammonium bromide to precipitate cleanly and in high yield from the reaction mixture as it is formed and thereby prevent further reaction.⁸ This procedure was less successfully extended to other adducts including trimethylphosphonium, pyridine and picolyl derivatives. Synthesis of the corresponding bifunctional resin involves coupling of the precursor to a base resin poly(4-vinylpyridine) with variable crosslinking.

We have synthesized and determined Pu(IV) distribution coefficients (K_d) onto several 'systematic series' of mono- and bifunctional resins to examine the effects of varying the following conditions:

- 1) The chemical structure of the second cationic site: pyridinium > trimethylphosphonium > trimethylammonium (Figure 4).
- 2) The length and chemical structure of the spacer between the two cationic sites: generally a 4-5 atom spacer is optimal for plutonium uptake (Figure 4).
- 3) The percent crosslinking of the substrate: decreasing the crosslinking from 25% to 18% yields a ca. 50-100% increase in K_d with little impact upon resin stability (Figure 5).
- 4) The percent derivatization: performance increases with greater derivatization up to 100% (Figure 5).

The plutonium sorption behavior depicted in Figure 4 has been discussed in publications^{9,10} and is a primary component in the development of molecular models for the electrostatic interactions between the $\text{Pu}(\text{NO}_3)_6^{2-}$ dianion and the dicationic sites¹¹ as described later in the modeling section. In general, it appears that there is an optimal 'bite size' for electrostatic interactions between the $\text{Pu}(\text{NO}_3)_6^{2-}$ dianion with the two cationic sites in a fashion analogous to that found in covalent bonding interactions. A very short 'spacer' length provides a site that is too hindered for optimal interactions with the dianion and exhibits kinetic hindrances as well. Once the spacer length increases beyond an 'optimal' 4-5 - CH_2 - units, entropic disadvantages develop, causing a decrease in binding.

Figure 4. 30 min K_d vs. Spacer length for 402 -- class of resins



Although the 402 class of polyvinylpyridine bifunctional resins exhibit extremely high plutonium affinity and rapid sorption kinetics, this low-crosslinked material is not suitable for the large-scale column applications. In collaboration with Reilly Industries (manufacturers of

Reillex HPQ), we developed similar resins (both methylated to compare directly with HPQ and bifunctional) based on more rigid macroporous polyvinylpyridines with 18, 21 and 25% divinylbenzene crosslinking agent. Also, the percentage of pyridine sites of the base resin that were derivatized was varied. As seen in Figure 5, the bifunctional resins consistently outperform the monofunctional resins and decreasing the percentage of crosslinking agent has a positive impact on plutonium sorption.¹² Although the bifunctional resin cannot be derivatized as highly as the methylated resins (probably due to some sites being inaccessible to the larger derivatizing agent), performance increases sharply between about 50 and 70% whereas it remains nearly constant above ~40% for the methylated resins.

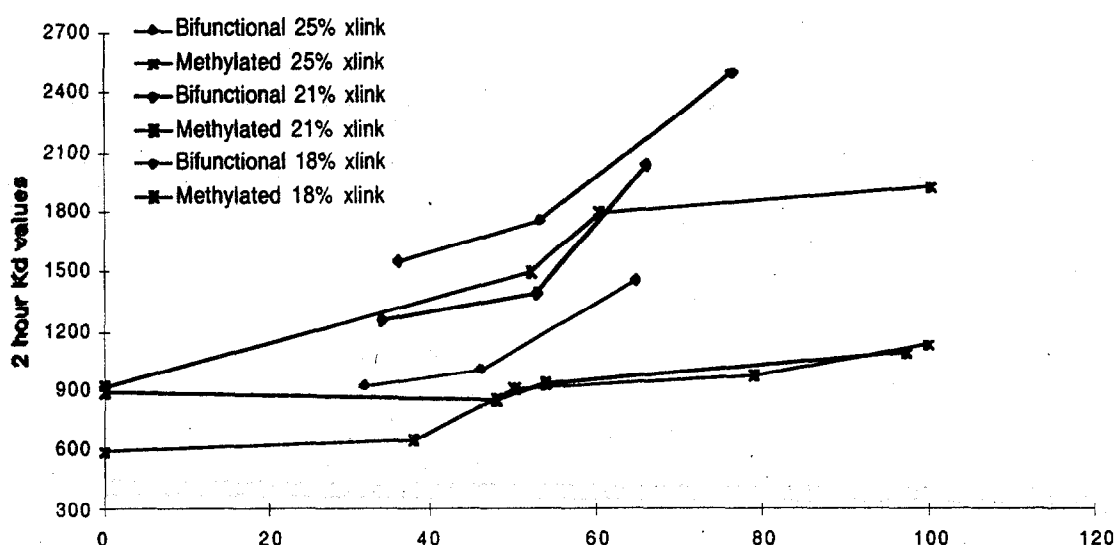


Figure 5. K_d vs. percent functionalization by % crosslinked base-resins
Methylated resin = N-methylated polyvinylpyridine
Bifunctional = Polyvinylpyridine N-alkylated with $-(CH_2)_3N(CH_3)_3$

We have also synthesized a number of *soluble* anion-exchange polymers based on linear poly(4-vinylpyridine) and developed spectroscopic methods to determine plutonium distribution coefficients.¹³ The evolution of these materials was motivated by our desire to decouple the effects of solution-to-solid phase-transition energies and kinetics from the smaller free energy changes of exchanging a nitrate anion for an anionic plutonium complex. Our models (discussed below) focus on the *differences* in electrostatic attraction observed for the $Pu(NO_3)_6^{2-}$ anion within a series of resins with variable 'spacer' lengths between the two cationic sides. Without specific values for the energy of phase-transfer, we are forced to assume that this energy term is constant within a series (i.e. $\Delta E_{PT} = 0$). While this assumption is not unreasonable, it is risky in that the energies of phase-transfer from solution to solid are significantly greater than the energies

of electrostatic attraction. Thus, even small variations in ΔE_{PT} could bias our calculations. Plutonium distribution coefficients for various mono- and bi-functional resin analogues are presented in Figure 6.

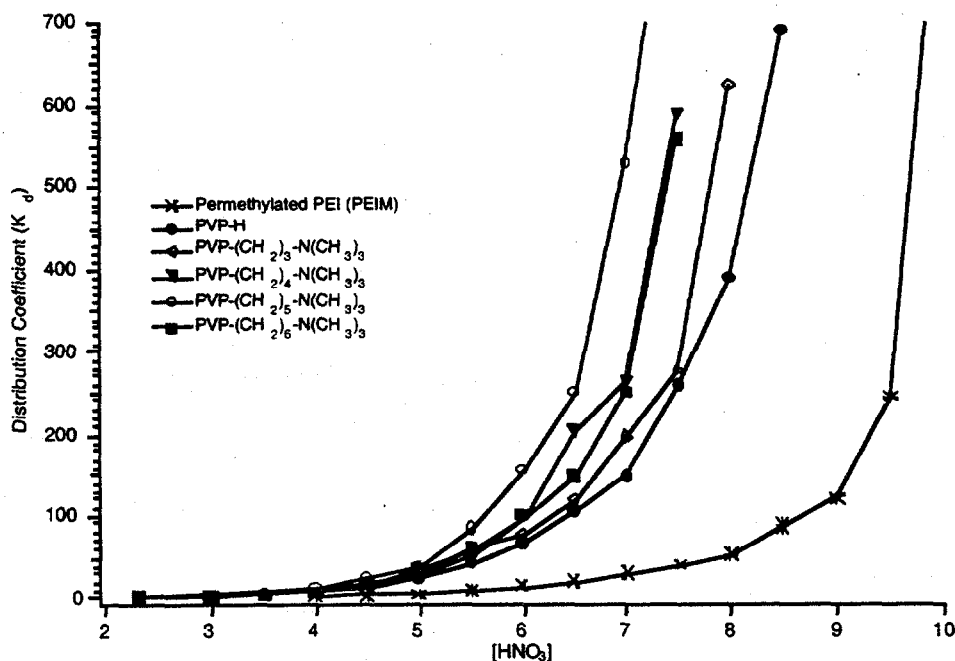


Figure 6. Pu(IV) distribution coefficient vs. nitric acid concentration for selected monofunctional and bifunctional PVP polymers and permethylated PEI in 7.0M HNO₃.

Normally, this type of information would be derived from liquid-liquid extraction studies, but development of appropriate dicationic extractants was problematic due to solubility issues. Through the use of aqueous soluble anion-exchange polymers, however, we have determined that overall plutonium affinity for the anion-exchange sites in the soluble polymers is much lower than for comparable solid resins (as expected for the lower ΔE_{PT}), but the K_d values exhibit the very similar trends in that bifunctionalized materials are superior to monofunctionalized (Figure 6) and a five-atom 'spacer' between the two cationic sites is superior to shorter spacers (Figure 7). Thus, we are more confident that the experimental data from Pu(IV) sorption onto solid-phase resins are appropriate to use to evaluate our electrostatic models.

Modeling and design activities: We have developed MM2 parameters for Pu, U, Th and Np(IV) nitrate systems. Using these parameters, we can model the nitrate-actinide bonding interactions. Determination of the charge distribution of the hexanitrate dianions was problematic because of the exceptionally high orbital degeneracy of the complex. We developed a 'theoretical model' compound, the Pu(NO₃)₃ triradical, for which partial charges could be

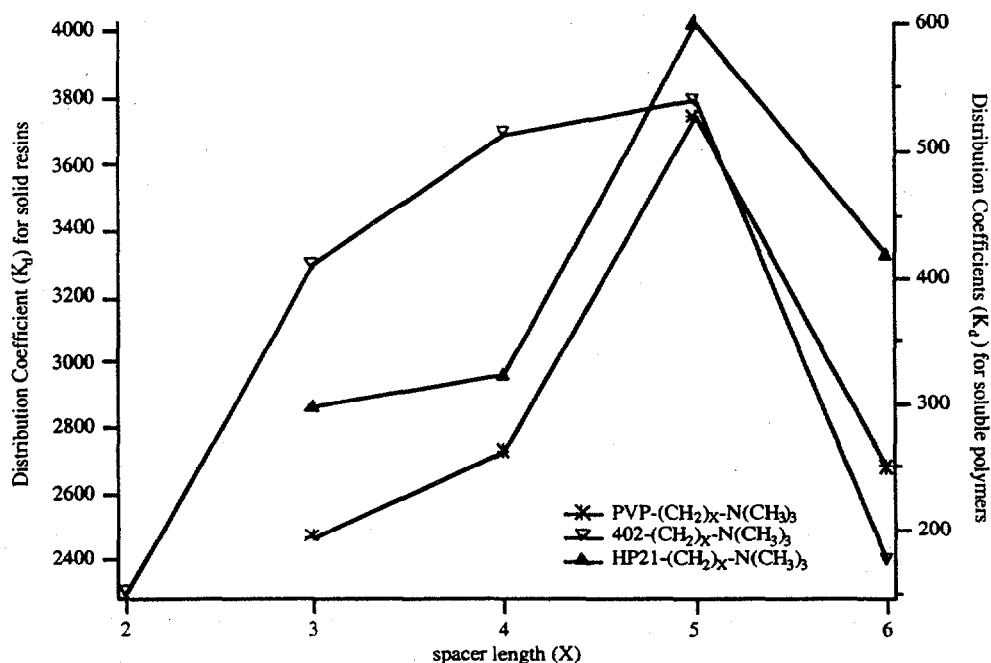


Figure 7. Pu(IV) distribution coefficients for solid (left axis, 6 hrs) and soluble (right axis, equilibrium) polymers.

determined using *ab initio* calculations. Later calculations of the analogous thorium hexanitro complex confirmed the efficacy of this model.

Optimized anion/cation configurations were determined using HyperChem's MM+. This program is very efficient in modeling steric interactions and has been shown to be both fast and accurate at modeling both actinide complexes and organic systems.¹⁴ The optimized ion-pair configuration was selected from energy-minimized structures generated from various initial configurations. Figure 8 presents an energy-minimized interaction between the plutonium hexanitrate dianion and the free analogue of the resin with a 1,4-butylene spacer and trimethylammonium terminus.

Summing all the electrostatic effects between all the atoms in intermolecular systems was done *via* dynamic data exchange (DDE) with Microsoft's Visual C++ 5. In equation 1, the Stickiness Factor (SF) is defined as the sum of the intermolecular electrostatic moments where i and k are the molecule index, j and l are the atoms inside molecule i and k respectively (as assigned by HyperChem), q is the charge on the atom, and r is the distance from atom(i,j) to atom(k,l) in Å.

$$SF \equiv \frac{1}{2} \sum_{i \neq k} \frac{q(i,j) \cdot q(k,l)}{r((i,j)(k,l))} \quad eq.1$$

Stickiness Factor values for ion pairs were calculated using partial and formal charge metrics. When using formal-charge metrics, summation of the electrostatic charge interactions is greatly simplified by the number of atoms with zero charge.

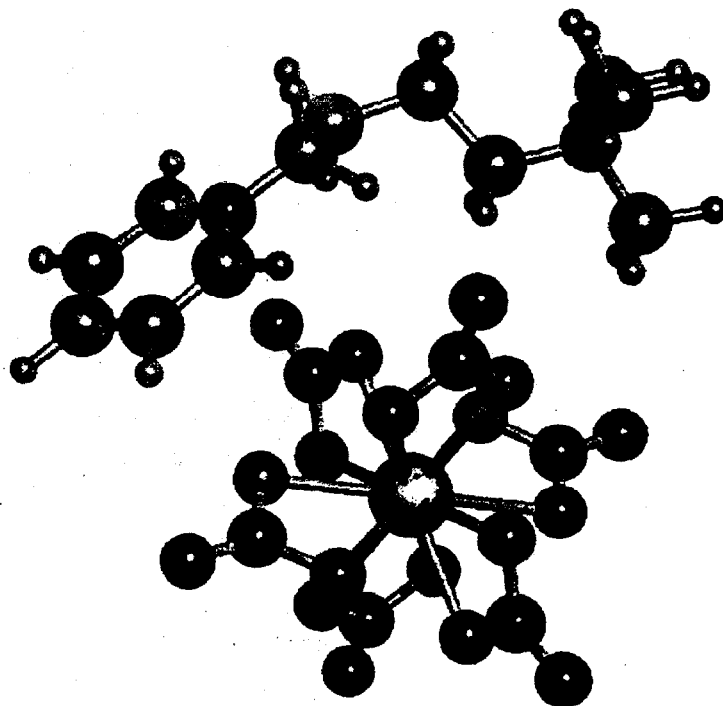


Figure 8. Energy-minimized structure of the plutonium hexanitrate dianion with a free analogue of the pyridinium-based resin with a butylene spacer and a trimethylammonium cationic site.

Via calculation of the electrostatic interactions (called 'stickyness factor' or SF) between the Pu-hexanitrate dianion and the dicationic "resin site", we have correlated SF with experimental K_d s for three series of resins. Correlation of SF with K_d for the corresponding resin was determined by plotting the experimental K_d values versus the calculated SF values for each ion pair within a series, then applying a simple linear fit (Figure 9). While thermodynamic equations predict an exponential fit ($K_d = e^{-\Delta G/RT}$), e to a very small number is essentially linear.

Linear correlation coefficients (r) were similar for $\ln K_d$ vs. SF and K_d vs. SF plots. The correlation between SF and K_d has a negative slope, reflecting the hypothesized relationship between the force of electrostatic attractions (a more negative value indicates a stronger attractive force) and the affinity of the dicationic site for the plutonium hexanitrate dianion (a more positive K_d indicates greater plutonium uptake from solution). Correlation values are reported as r^2 .

Calculated K_d values are derived from the empirical linear correlation. It is, admittedly, a circular process and, at this point, only an alternative way of viewing the goodness-of-fit and of extrapolating predicted K_d values to a longer spacer group than we currently have experimental data to support. An *a priori* determination of K_d values from the SF values between series of resins would require knowing the slope and intercept for each type of functional group - a

capability we have not yet developed. The intercept value is most probably related to the magnitude of the TdS term of G, and we will continue to pursue methods for determination of this term. However, the straightforward determination of *which* member of a *series* would display the best distribution values can be extracted directly from the SF values.

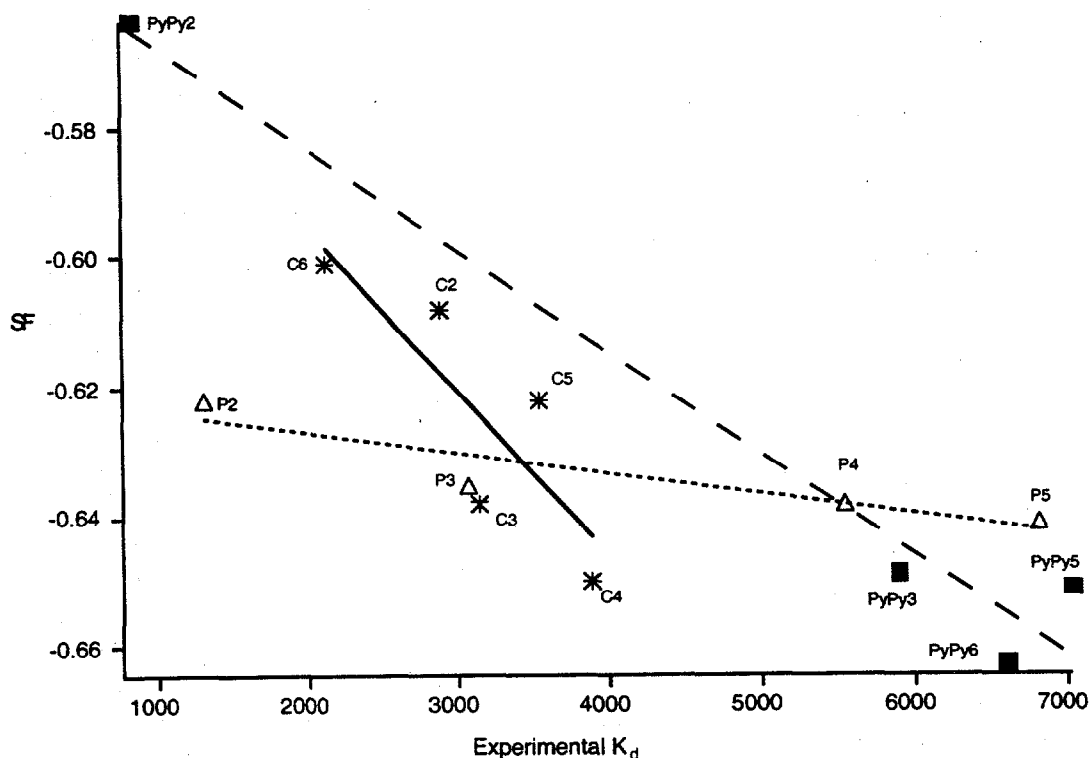


Figure 9. Stickness factor (SF) versus experimental Pu(IV) distribution coefficients (K_d) for ion pairs for three series of dications using formal charge metrics. Dication names are abbreviated as follows: Cx is $[C_5H_5N(CH_2)_xN(CH_3)_3]^{2+}$ (solid line), Px is $[C_5H_5N(CH_2)_xP(CH_3)_3]^{2+}$ (dotted line), and PyPyx is $[C_5H_5N(CH_2)_xC_5H_5N]^{2+}$ (dashed line).

Americium removal from waste solutions

The aging of the U. S. nuclear stockpile presents a number of challenges, including the ever increasing radioactivity of plutonium residues due to the ingrowth of Am-241. Minimization of this weak gamma-emitter in process and waste solutions is desirable to reduce both worker exposure and the effects of radiolysis on the final waste product. Here, we summarize efforts to reduce the total decay-heat in cemented wastes by removing americium from nitric acid processing solutions. A procedure that reliably removes 75% of the activity from cemented wastes would provide compliant drums, as well as help the Plutonium Facility meet mandated waste reduction targets.

We investigated parameters that affect the sorption of Am(III) onto anion-exchange resins from concentrated effluents derived from nitric acid processing of plutonium residues.^{6,7} Varied parameters include the nitrate salt concentration and composition and the nitric acid concentration. These post-evaporator wastes are nearly saturated solutions of acidic nitrate salts, and americium removal is complicated by physical factors, such as solution viscosity and particulates, as well as by the presence of large quantities of competing metals and acid. We find that under these extremely concentrated conditions, Am(III) removal efficiencies can surpass 50% per contact. Distribution coefficients for americium are insensitive to solution acidity and appear to be driven primarily by low water activities of the solutions.

Table 1 summarizes a single/double batch contact experiment with authentic evaporator bottoms. We consider the total alpha-activity removal from the second contact to be most indicative of Am(III) sorption since all materials have sufficient capacity and affinity for near-quantitative Pu(IV) uptake in the first contact. Small column experiments definitely showed that the experimental bifunctional anion-exchange resins were superior to the commercially-available HPQ-100 in both retention and elution profiles.

We conducted a process-scale evaluation for the treatment of evaporator bottoms by anion-exchange using an existing 10-L column of older Reillex HPQ (~70% derivatized). This column, as well as others in the TA-55 Plutonium Facility, has been in use for several years with very little degradation of sorption kinetics or capacity. The 50-L of evaporator bottoms were in

	First Contact 100 mg resin	Second Contact 100 mg resin	Net ^a
HPQ-100	61 %	73 %	90 %
HP18-Me	64 %	72 %	90 %
HP25-(CH ₂) ₅ -N(CH ₃) ₃	67 %	82 %	94 %

^a Calculated from final vs. initial alpha activity

Table 1. Alpha-activity removal from evaporator bottoms. Initial activity ~ 1.44 x 10⁹ dpm/mL, ~0.129 g/L Am (65% of a activity), ~2.95 g/L Pu (35% of a activity).

two 25-L batches. The first feed solution (F#1) had very low Pu and Am content (Pu=0.229 g/L, Am= 0.029 g/L), the second batch (F#2) was closer to average (Pu=1.33 g/L, Am=0.082 g/L). Both had titrated acid concentrations of slightly less than 1 M. At the end of the 50 L of feed through the Reillex HPQ column, the gamma activity from americium in the effluent was still well below either feed activity. Americium and plutonium distributions into the various solution fractions as determined from final solution analyses (gamma) are reported in Table 2. This level of Am(III) retention is sufficient to meet heat-loading requirements in most situations.

From a practical viewpoint, the modest americium removal needs (ca. 50-75%) from evaporator solutions allow sufficient latitude for the use of non-optimized conditions, such as running existing columns filled with older, well-used Reillex HPQ. Newer materials, such as HPQ-100 and the experimental bifunctional resins, which exhibit higher distribution coefficients, would allow for either increased Am removal or the use of smaller columns. Improvements in the real-time, in-line gamma analysis available for the process-scale operations could provide sufficiently accurate and responsive data to allow for proper partitioning of the effluents into a fraction for cemented waste and a fraction for Am/Pu precipitation.

	Feed (ave) 50 L	Effluent of F#1, F#2 45 L	Wash 15.2 L	Eluate#1 20.4 L	Eluate#2 15.5 L	Mass balance (%)
Am (g/L)	0.056	0.00752	0.0268	0.0912	0.00686	
Pu (g/L)	0.79	0.531	0.0470	1.36	0.403	
Am (g)	2.79	0.34	0.41	1.86	0.11	
Pu (g)	39.8	23.9 ^a	0.7	27.7	6.3	
Am (%)	-	12.2	14.6	66.7	3.9	97.4
Pu (%)	-	60.0 ^a	1.8	69.6	15.7	147.1 ^a

^a Includes residual Pu mobilized from the column

Table 2. Americium and plutonium concentrations and total mass as a function of process fraction.

Miscellaneous activities

Other metals of interest to both EM and to the commercial sector include technetium and chromium. Both of these metals tend to exist as oxoanions in environmental samples – pertechnetate (TcO_4^{1-}) and chromate (CrO_4^{2-}). Our experimental bifunctional resins showed only marginal enhancement for the uptake these oxyanions over conventional anion-exchange materials. This lack of enhancement is not surprising give that these oxyanions are considerably smaller in diameter than the Am or Pu nitrate complexes for which the bifunctional resins were optimized.

However, for the divalent precious metal complexes PtCl_4^{2-} and PdCl_4^{2-} , the experimental bifunctional resins exhibit a singularly high level of dianion affinity. Again, as with the Pu and Am complexes, there appears to be some size preference for the resin with a 4-5 carbon spacer distance between the two cationic sites. The large difference in sorption behaviour between Pt(II) and Pt(IV) demonstrated in Figure 10 suggests that platinum may be recovered from the

resin using a strong oxidant. These polyvinylpyridine-based resins are extremely resistant to oxidative degradation.

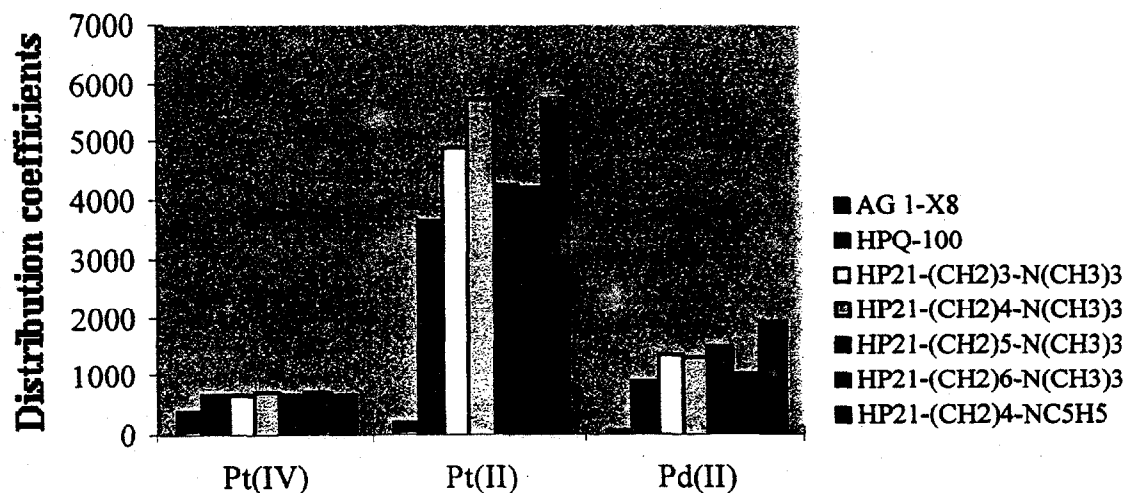


Figure 10. Precious metal uptake onto anion-exchange resins

Relevance, Impact and Technology Transfer

- a. The concepts and new materials developed by this EMSP project address critical needs within DOE Environmental Management programs to remove radionuclides and other metal ions more efficiently from a variety of waste and process streams. Ion exchange is a well-established, robust process used widely in DOE and industrial facilities. Development of more selective ion-exchange materials will help reduce operating costs and minimize waste from processing operations that treat a wide variety of EM residues and wastes, remediate environmental contamination, and decontaminate and decommission facilities. The focus areas where applications can be anticipated include Tanks, Plutonium, Mixed Waste, Decontamination & Decommissioning, and Subsurface Contaminants. Some potential applications are briefly mentioned in the Research Objectives.
- b. More rapid development and deployment of selective ion-exchange systems has wide applicability to processes needed for treatment of EM residues, wastes, and contaminated sites and facilities. More selective and efficient ion exchange systems can provide faster throughput rates, reduced wastes, and lower capital equipment costs. A good example is provided by the project described above for testing the removal of americium from high nitrate evaporator bottoms. Removal of americium activity from the final cemented waste drum was required to meet DOE compliance requirements for shipment to WIPP. The new

anion-exchange materials tested could reduce the cost of this operation by allowing higher throughputs with the same volume of resin.

- c. This project has developed significant new fundamental knowledge that advances our ability to design improved ion-exchange systems more rapidly, but also has provided new materials that have applications in the near term. One patent has been issued on these new anion exchange materials, another patent is expected to issue in the near future, and a patent disclosure is presently being evaluated by the Laboratory. A licensing agreement has been signed with an industrial firm to develop commercial applications of these new materials. Thus the project has effectively bridged the gap between fundamental research and needs-driven applied technology development.
- d. As noted above, a licensing agreement is in place with Reilly Industries, Inc., to develop commercial applications of the new anion exchange materials synthesized and tested in this project. Thus, we feel that the results of this EMSP project will be used. The first users would likely be industrial customers of Reilly Industries, but the new materials would be available at essentially the same time for DOE applications. DOE customers that are likely to deploy these new anion exchangers as they become available include actinide processing operations at the Savannah River Site and Los Alamos National Laboratory.
- e. Larger scale preparations of the new materials are underway at Reilly Industries to allow for testing in various industrial applications.
- f. The new scientific knowledge generated in this project advances our ability to design improved ion-exchange systems using calculational methods to narrow the range of materials that must be synthesized and tested. Professor Bartsch and his group at Texas Tech University and our team at Los Alamos have developed considerable expertise in preparing multifunctional polymers. Some of this expertise has been transferred under the licensing agreement to Reilly Industries.
- g. As noted above, this project advances our ability to design improved ion-exchange systems using calculational methods to narrow the range of materials that must be synthesized and tested. The concept of preorganizing a multifunctional anion exchange site to obtain improved selectivity has been validated and some specific synthetic routes to new materials of this type have been developed.
- h. More selective ion-exchange materials will have wide application in industry and it is really the industrial markets that will drive the commercial manufacture of new ion exchangers that can be used in DOE operations. Most DOE applications are too small to give industry the incentive to manufacture new products for DOE alone. For example, the new anion-exchange materials developed in this EMSP project are under investigation by Reilly Industries, Inc., for a variety of industrial applications under a licensing agreement with the Laboratory. New

commercial anion-exchange resins developed by Reilly under this agreement will then be available for purchase and use at Savannah River, Los Alamos, and other DOE sites.

- i. As noted above, a licensing agreement is in place with Reilly Industries, Inc., Indianapolis, IN to develop commercial applications of the new materials. The technical contact at Reilly is Don McQuigg (phone: 317-247-8141, e-mail: dmcquigg@reillyind.com) and the marketing contact is Michael Marlo (phone: 317-248-6537). The Savannah River Technology Center has also expressed interest in the new anion-exchange systems. The contact at SRTC is Dr. Major C. Thompson (phone: 803-725-2507, e-mail: major.thompson@srs.gov).

Project Productivity

Significant project accomplishments (to date)

- 1) Patent has been obtained for some of the new anion-exchange polymers materials developed. A second patent application is in progress and the patent is expected to issue in late 2000 or early 2001. A patent disclosure for the new water-soluble polyvinylpyridine polymers developed has been filed.
- 2) Licensing/marketing agreement with Reilly Industries, Inc., Indianapolis, IN, for the commercialization of the new anion-exchange materials has been completed.
- 3) Experimental resins have proven effective at removal of Am(III) from high salt/ high acid evaporator waste at LANL to meet regulatory disposal requirements. Selected as one of DOE-AL "success-stories" for FY98.
- 4) Have firmly established a link between molecular mechanics-determined parameters, *ab-initio* - determined energy terms and experimentally-determined distribution coefficients. This link effectively allows us to pre-determine optimally-arranged anion-exchange sites.
- 5) The basic research/ applied systems approach for this project has been featured in LANL's Actinide Quarterly magazine and in several division-wide technical reviews.
- 6) The new bifunctional resins show promise for small-scale, rapid-throughput processing of Pu-238 scrap.

Status of the original project milestones

Year 1 (FY 97)

- Complete actinide speciation analysis for actinides in nitrate solutions - *completed*
- Complete synthesis of a systematic series of bifunctional poly(4-vinylpyridine) polymers, complete testing of the radionuclide sorption properties of these materials - *completed*
- Synthesize a partial set of the multifunctional extractants for structural and speciation studies - *completed*

- Develop molecular modeling parameters for relevant actinide complexes - *completed*

Year 2 (FY98)

- Perform actinide speciation analyses for actinides in chloride and carbonate solutions - *completed*
- Complete synthesis of a systematic series of bifunctional polystyrene polymers, complete testing of the radionuclide sorption properties of these materials - *completed*
- Synthesize and evaluate a partial set of the multifunctional extractants - *dropped*
- Refine molecular modeling parameters for radionuclide/functional site interactions - *completed*

Year 3 (FY99-00)

- Complete speciation analyses for actinides in chloride and carbonate solutions, examine other relevant media - *incomplete*
- Complete synthesis and evaluation of the multifunctional resins - *dropped*
- Complete synthesis and evaluation of the multifunctional extractants - *dropped*
- Prepare final molecular modeling parameters for radionuclide/functional site interactions - *completed*
- Decision point for implementation plan for facilitate uptake methodology - *in progress*
- Work with industrial partners in commercialization plan for new materials - *in progress*

Personnel Supported

11 university - 8 graduate students, 2 postdoctoral assistants, one faculty

Results obtained while supported by the DOE-EMSP grant will be incorporated into the theses and/or dissertations of 2 of the TTU graduate student coworkers.

6 LANL – 5 technical and support staff, 1 postdoctoral associate

Publications

Published publications in peer-reviewed journals

"New Bifunctional Anion-Exchange Resins for Nuclear Waste Treatment" Marsh SF, Jarvinen GD, Bartsch RA; *Reactive Polymers* 1997, 35, 75-80.

"New Bifunctional Anion-Exchange Resins for Nuclear Waste Treatment-II" Marsh SF; Jarvinen, GD, Bartsch RA, Nam J, Barr ME; *J. Radioanal. Nucl. Chem.* , 1998, 235, 37-40.

"Facile synthesis of (omega-bromoalkyl) trimethylammonium bromides" Bartsch RA, Zhao W, Zhang ZY; *Synthetic Communications*, 1999, 29(#14), 2393-2398.

Technical reports & publications

- "Molecular-engineered resins for plutonium recovery" Marsh SF, Viers DK, Jarvinen GD, Barr ME, Moody EW; LA-UR-00-2441, Los Alamos Science Magazine, 2000.
- "Americium separations from high salt solutions" Barr ME, Schulte LD, Jarvinen GD, Espinoza J, Ricketts TE, Valdez Y, Abney KD, Bartsch RA, Chamberlin RM; Los Alamos Unclassified Publication, LA-13676-MS, March 2000.
- "Sorption of Pu(IV) from nitric acid by bifunctional anion-exchange resins" Bartsch RA, Chamberlin RM, Marsh SF, Barr ME, Jarvinen GD, Zhao W, Elshani S, Zhang ZY; Amarillo National Resource Center for Plutonium, TX, ANRCP-99002708, DE99002708, 1999.
- "New anion-exchange polymers for improved separations" Jarvinen GD, Marsh SF, Barr ME; Los Alamos Unclassified Report, LA-UR-97-2048, 1997.
- "TRU Evaporator Bottom Waste", Barr ME, Los Alamos Unclassified Report, LA-UR-97-4306, Oct. 1997.

Publications (submitted or in preparation)

- "Americium separations from nitric acid process effluent streams" Barr ME, Schulte LD, Jarvinen GD, Espinoza J, Ricketts TE, Valdez Y, Abney KD, Bartsch RA; accepted in *Journal of Radioanalytical and Nuclear Chemistry*, Marc V Conference, Kona, Hawaii , April 2000.
- "QSAR of Distribution Coefficients for $\text{Pu}(\text{NO}_3)_6^{2-}$ Complexes using Molecular Mechanics" Moody EW, Barr ME, Jarvinen, GD; accepted in *Journal of Radioanalytical and Nuclear Chemistry*, Marc V Conference, Kona, Hawaii , April 2000.
- "Sorption of Pu(IV) from Nitric Acid by Bifunctional Anion-Exchange Resins" Bartsch, RA, Zhang ZY, Elshani S, Zhao W, Jarvinen GD, Barr ME, Marsh SF, Chamberlin RM; in preparation, to be submitted to *Separation Science and Technology*.
- "Plutonium (IV) Sorption by Soluble Anion-Exchange Polymers" Barr ME, Jarvinen GD, Moody EW, Vaughn RB, Bartsch RA, Silks LA; submitted to *Separation Science and Technology: Solvent Extraction and Ion Exchange*.
- "Americium Separations from High Salt Solutions using Anion Exchange" Barr ME, Jarvinen GD, Stark PC, Chamberlin RM, Bartsch RA; submitted to *Separation Science and Technology*.

Interactions

Presentations at national and international meetings and conferences

- "Americium separations from nitric acid process effluent streams" Barr ME, Schulte LD, Jarvinen GD, Espinoza J, Ricketts TE, Valdez Y, Abney KD, Bartsch RA; Fifth international

- conference on Methods and Applications of Radioanalytical Chemistry (Marc V), Kona, Hawaii , April 2000.
- "QSAR of Distribution Coefficients for $\text{Pu}(\text{NO}_3)_6^{2-}$ Complexes using Molecular Mechanics" Moody EW, Barr ME, Jarvinen, GD; Fifth international conference on Methods and Applications of Radioanalytical Chemistry (Marc V), Kona, Hawaii , April 2000.
- "Molecular modeling of anion-exchange sites" Barr ME, Jarvinen GD, Moody EW; LA-UR-00-0592, Chemistry for a Cleaner Environment Conference, Santa Fe, NM, Jan. 2000.
- "New anion-exchange resins for improved separations of nuclear materials" Barr ME, et.al, Chemistry for a Cleaner Environment Conference, Santa Fe, NM, Jan. 2000.
- "New anion-exchange resins for improved separations of nuclear materials" Barr ME, Jarvinen GD, Marsh SF, Moody EW, Chamberlin RM, Bartsch RA, Zhao WY; Abstracts of Papers of the American Chemical Society , v. 218(pt.1) pp. 107-NUCL Aug. 22, 1999
- "Americium Separations from Complex Mixtures using Anion Exchange" Barr ME, Jarvinen GD, Schulte LD, Stark PC, Chamberlin, RM; Abstracts of Papers of the American Chemical Society, v. 217 pp. 019-IEC March 21, 1999.
- "Sorption of Pu(IV) from Nitric Acid by Bifunctional Anion-Exchange Resins" Bartsch, RA, Zhang ZY, Elshani S, Zhao W, Jarvinen GD, Barr ME, Marsh SF, Chamberlin RM; Abstracts of Papers of the American Chemical Society, v. 217 pp. 125-IEC March 21, 1999.
- "QSAR of distribution coefficients for actinide hexanitrate complexes" Moody EW, Barr ME, Jarvinen GD; Abstracts of Papers of the American Chemical Society, v. 217(pt.2) pp. 170-NUCL March 21, 1999.
- "Actinide Decontamination of Nitric Acid Process Effluents", Schulte LD, Barr ME, Abney KD, Espinoza JM, Chamberlin RM, LA-UR-99-2427, 1999 NMT Division Review, May 1999.
- "Molecular Modeling Insights into Waste Disposition", Moody EW, Barr ME; LA-UR-98-4871, Idaho National Engineering Laboratory, Nov. 1998.
- "Sorption of Pu(IV) by Soluble Anion-Exchange Polymers", Barr ME, Jarvinen GD, Moody EW, Vaughn RB; Abstracts of Papers of the American Chemical Society, v. 216(pt.2) pp. 88-NUCL AUG 23, 1998, and v. 216(pt.1) pp. 5-TECH AUG 23, 1998
- "Development of Anion-Exchange Resins for Separations of Actinides", Barr ME, Jarvinen GD, Marsh SF, Bartsch RA; Abstracts of Papers of the American Chemical Society, v. 213(pt.2) pp. 73-IEC APR 13, 1997
- "New Bifunctional Anion-Exchange Resins for Nuclear Waste Treatment", Marsh SF, Jarvinen GD, Bartsch RA, Nam J, Barr ME; Marc IV conference on Radioanalytical Chemistry, Kona, HI, April 1997.

Consultations

"Effluent Polishing Techniques for Nitrate Operations", Schulte LD, Barr ME, Abney KD, Espinoza JA, French/US Technical Exchange – Valduc and JOWOG 22-2 Meeting- Aldermston, LA-UR-98-4522, Oct.1998.

Collaborations

Materials licensing and marketing agreement with Reilly Industries for production & marketing of new resins.

Transitions

A licensing agreement is in place with Reilly Industries, Inc. to develop commercial applications of the new anion exchange materials synthesized and tested in this project. Thus, we feel that the results of this EMSP project will be used. The first users would likely be industrial customers of Reilly Industries, but the new materials would be available at essentially the same time for DOE applications. DOE customers that are likely to deploy these new anion exchangers as they become available include actinide processing operations at the Savannah River Site and Los Alamos National Laboratory.

Patents

US5670550: "Ion exchange polymers for anion separations"; Issued/Filed Dates: Sept. 23, 1997 / June 7, 1995; Application Number: US1995000476964

This patent was initiated prior to funding under this EMSP project, but covers the applications investigated.

Application Number: EP830388A1: "Ion exchange polymers for anion separations"

Patent Disclosure: "Soluble Anion-Exchange Polymers"

Future Work

Development of in-house and commercial uses for these resins. Application of R&D100.

Appendices

Published and submitted manuscripts

Literature Cited

- 1) Marsh, S. F.; Day, R. S.; Veirs, D. K. "Spectrophotometric Investigation of the Pu(IV) Nitrate Complex Sorbed by Ion Exchange Resins," Los Alamos National Laboratory, 1991.
- 2) Viers, D. K.; Smith, C. A.; Berg, J. M.; Zwick, B. D.; Marsh, S. F. *Journal of Alloys and Compounds* 1994, 213/214, 328-332.

- 3) Allen, P. G.; Veirs, D. K.; Conrandson, S. D.; Smith, C. A.; Marsh, S. F. *Inorganic Chemistry* **1996**, *35*, 2841-2845.
- 4) Berg, J. M.; Veirs, D. K.; Vaughn, R. B.; Cisneros, M. A.; Smith, C. A. *Journal of Radioanalytical and Nuclear Chemistry* **1998**, *235*, 25-29.
- 5) Berg, J. M.; Veirs, D. K.; Vaughn, R. B.; Cisneros, M. R.; Smith, C. A. *Applied Spectroscopy* **2000**, *54*, 812-823.
- 6) Barr, M. E.; Jarvinen, G. D.; Stark, P. C.; Chamberlin, R. M.; Bartsch, R. A.; Zhang, Z.-Y.; Zhao, W. *submitted to J. of Separation Science and Technology* **2000**.
- 7) Barr, M. E.; Schulte, L. D.; Jarvinen, G. D.; Espinoza, J.; Ricketts, T. E.; Valdez, Y.; Abney, K. D.; Bartsch, R. A. *accepted to Journal of Radioanalytical and Nuclear Chemistry* **2000**.
- 8) Bartsch, R. A.; Zhao, W.; Zhang, Z. Y. *Synthetic Communications* **1999**, *29*, 2393-2398.
- 9) Marsh, S. F.; Jarvinen, G. D.; Bartsch, R. A. *Reactive and Functional Polymers* **1997**, *35*, 75-80.
- 10) Marsh, S. F.; Jarvinen, G. D.; Bartsch, R. A.; Nam, J.; Barr, M. E. *Journal of Radioanalytical and Nuclear Chemistry* **1998**, *235*, 37-40.
- 11) Moody, E. W.; Barr, M. E.; Jarvinen, G. D. *accepted to Journal of Radioanalytical and Nuclear Chemistry* **2000**.
- 12) Bartsch, R. A.; Barr, M. E.; Jarvinen, G. D.; Marsh, S. F. *for submission to Separation Science and Technology* **2000**.
- 13) Barr, M. E.; Jarvinen, G. D.; Moody, E. W.; Vaughn, R.; Silks, L. A.; Bartsch, R. A. *submitted to Journal of Separation Science and Technology* **2000**.
- 14) Allinger, N. L.; Burket, U. *Molecular Mechanics, ACS monograph series 177*; Allinger, N. L.; Burket, U., Ed.; American Chemical Society: Washington, DC, 1982.

